The Role of Hydrophility and Organophility in the Movement of Toxic Elements in Soils

L. HARGITAI

University of Horticulture and Food Industry, Budapest

Introduction

Some years ago a new research project was started dealing with heavy metal contaminations and their distribution in soil profiles. The investigated areas were the North and Central Transdanubian and the North-Eastern industrial districts of Hungary. At the same time investigations were made on the effect of organic materials and soil humic substances on the mobility of heavy metals. The present studies were based on some of the results obtained on the organophility of toxic heavy metals, especially Pb, Ni, Cd and Hg.

In previous long-term experiments on brown forest soils various doses of sewage sludge were applied. The mobility of the accumulated heavy metals was investigated after 10 years. The amounts of toxic elements applied were 24 times greater at the highest rate of sewage sludge application than at the lowest rate. The influence of organic matter from the humus content of the soils or from doses of organic matter added to the soils with sewage sludge decreased the mobile amounts of toxic heavy metals according to their organophility, by 83% for Ni, by 76% for Pb and by 50% for Cd (HARGITAI, 1989, 1990).

Based on these results, in the present investigations the mobility of the main toxic elements was studied in connection with their binding through their organophility. At the same time it seemed to be of outstanding interest to carry out separate investigations on the hydrophility of some organophilic elements.

It is well-known that besides organophility, hydrophility is the other general factor influencing the mobility of toxic elements in the soils and in the entire environment. Many results about the movement of toxic heavy metals have been published in recent years (BERNHARD et al., 1986). This reflects the importance of their distribution in the environment, from the point of view of human health.

The concept of "chemical speciation", which has a great influence on the movement and distribution of toxic elements in the soils and in the environment has been investigated by many authors in the recent years (BERNHARD et

al., 1986; XU & ALLARD, 1991). The form of special chemical compounds and their chemical reactions expressed in the concept of chemical speciations is perhaps of interest for the movement of a group of toxic heavy metals, primarily Cd, Hg and As (XU et al., 1991; WILKEN & HINTELMANN, 1991), through their great affinity to develop metal-organic compounds. At the same time these metal-organic compounds are water-soluble, so they play a great role in the hydrophility of these elements (WILKEN & HINTELMANN, 1991; SCHUSTER, 1991).

In the present work the following main questions were investigated:

1. The general concept of the organophility of certain elements was first established in GOLDSCHMIDT's classical work (1937) about the organophility of some elements in geochemical processes. GOLDSCHMIDT's classical theory also mentions toxic heavy metals, which have recently played an outstanding role in environmental contamination, especially in soil contamination. An attempt has been made to investigate the differences in scale and character of the organophility of the elements Pb, Ni, Cd, Hg and As.

2. Based on the results, investigations were made on the influence and role of water on the movement of Hg in the environment from soils to groundwater and through water in the soils. Questions were also raised as to the nature and character of the hydrophility of Hg and As in their movement in the soil. In this connection one very interesting question seemed to be to what extent the interaction between organophility and hydrophility influences the movement of these toxic heavy metals in the soil.

3. The mobility of As is the third main question in this present work. It seems that the movement of As from its geochemical origin through the groundwater level to the soil is also influenced by chemical speciation and through organometal complexes from the interaction of As with organic ligands and humic substances. An attempt was also made to obtain some information about the binding of these elements to soil humic substances in connection with the extent of their organophility. The role of humus status (values were based on the amounts as well as the quality of humic substances) in the movement and binding of toxic heavy metals was expressed through this method as the environment protectional capacity of the soils (HARGITAI, 1983).

Materials and Methods

Investigations on the contamination of the soil with heavy metals were carried out within the framework of a project in which heavy metal contamination was investigated in soil profiles in the West Hungarian and North-East Hungarian industrial districts and also alongside the most important highways in the Transdanubian District (beside the M7 motorway). The elements investigated were the most important toxic heavy metals: Pb, Ni, Cd and Hg. Besides these,

As contaminations in the central southern part of the Great Hungarian Plain were also investigated, in the region between the Danube and the Tisza rivers. This territory is a sandy region with very deep-lying lowmoor peats between the sandy hills. The soils of this peatland area are the most As-contaminated soils in Hungary.

All the samples in the present investigations were collected from characteristic soil profiles. According to the character of the soils the investigations were conducted mainly in soil layers at a depth of 80-160 cm. Sampling was carried out in a sequence of 20 cm layers from the topsoils to the deepest layers. (Depending on the character of the profiles the thickness of the layers varied somewhat, but mostly averaged 20 cm.)

All the basic, characteristic soil parameters were determined from the samples: pH, $CaCO_3$ %, humus content as H % or as total organic matter content by loss of ignition in peats. In addition special investigations were made on humus conditions, so both the humus content and the stability coefficient of humic substances are expressed in the K value (HARGITAI, 1955). The nutrient supplies of the soils were also studied, especially the total N content, C/N ratio and the mobile N content, according to a seven-step continuous hydrolysis method. The first step is characteristic of mobile, available N, after hydrolysis in 0.25 *M* H_2SO_4 (HARGITAI, 1958).

Methods applied

Besides the common and usually applied methods such as pH, $CaCO_3$%, loss of ignition, etc., special investigations were carried out according to the following methods.

Humus quality through the determination of K values (HARGITAI, 1955): in this method air-dried, homogenized soil samples are investigated. 2 g of soil are placed in each 25 ml tube. 20 ml 1% NaF solution is added to one tube and 20 ml 0.5% NaOH solution to the other tube. The tubes are shaken by hand for 1-2 minutes and then left for 48 hours at room temperature. After filtering (MN 640 filter paper) the solutions are determined for their extinction values in the visible spectra at wavelengths between 420-725 nm. The extinction values determined in NaF solutions are divided by the extinction values in NaOH. The value calculated in this way is the Q value, which expresses the quantity of well-humified organic matter. The K value (humus stability value) is calculated from Q.

$$Q = \frac{E_{NaF}}{E_{NaOH}}$$

From these values it is possible to calculate the humus stability coefficients which are characteristic of humus quality.

$$K = \frac{E_{NaF}}{E_{NaOH} \cdot H}$$

The average of the K values at different wavelengths is characteristic of the humus quality of the investigated soils.

Higher K values show a better humus quality with many high molecular, well-humified humic substances. Raw organic materials without the development of characteristic humification processes or with slight humification are characterized by very low K values. From the H and K values it is possible to calculate the environment protectional capacities of soils in the following way.

$$EPC_G = D_x \cdot H^2 \cdot K$$

In this equation D_x is the thickness of the investigated soil layer, in cm. H is the total humus content of the soil layer, K is the above-mentioned stability coefficient of the humic substances.

The determination of the mobile amount of heavy metals in the soil layers is carried out by the extraction of soil samples with AcAA-EDTA according to the method of LAKANEN & ERVIÖ (1971), followed by the determination with atomic absorption spectrometry. The concentration of Hg contamination in the soil layers is determined in the same extract by the ICP method. The As concentrations in peats were determined by a treatment with "aqua regia": 3 parts cc. HCl + 1 part cc. HNO_3, and after this treatment the Hg concentration is determined by atomic absorption spectrometry.

Results and Conclusions

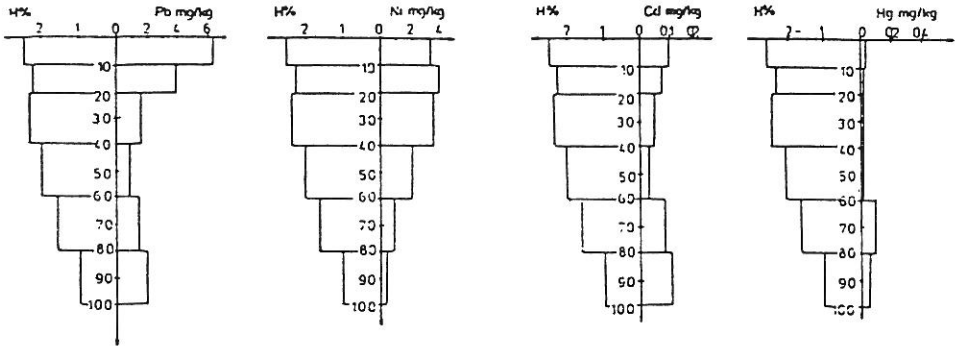
As a first step, in the investigations the heavy metal contamination in the soil was determined in the previously mentioned industrial areas. Some characteristic results are summarized in Table 1.

From Table 1 it can clearly be seen that the concentration with toxic heavy metals in the soil profiles shows some very interesting characteristics connected with the heavy metal distribution influenced by the humus layers of soil profiles and also with the influence of the groundwater level in the deeper layers. In profiles in which the groundwater level is close to 1 m (constant or periodically moving at this level) there is always an accumulation of Hg. This is also the case in soil profiles developed immediately from the river sediments of the Danube in profiles 4 and 5 or by Lake Bokod in profile 6, influenced by the groundwater level which is 1 m from the surface. In all these cases it can be

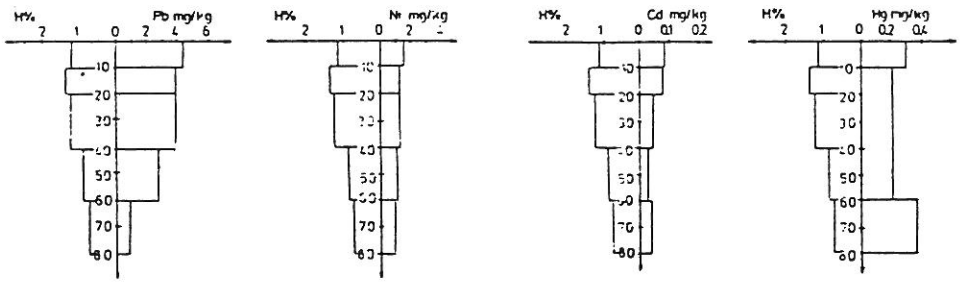
Table 1

The distribution of toxic heavy metal contaminations in soil profiles in the North Transdanubian and North East Hungarian Industrial District

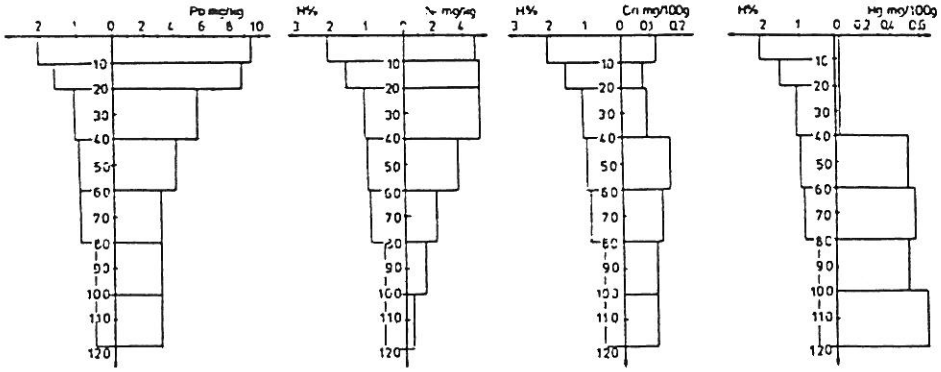
Site location	Depth of layer (cm)	Mobile amount of heavy metals, mg/kg soil			
		Ni	Pb	Cd	Hg
		Profile 1			
Near to the Danube	0-10	2.68	9.57	0.12	0.01
(about 400 m)	10-20	2.59	8.41	0.10	0.01
Tát-Nyergesűjfalu	20-40	2.64	10.02	0.14	0.01
(16 m from the road)	40-60	3.34	4.78	0.05	0.01
		Profile 2			
Near to Profile 1	0-10	2.69	7.87	0.10	0.01
nearer to the Danube	10-20	2.59	8.35	0.12	0.01
(25 m from the road)	20-40	3.21	2.91	0.02	0.01
	40-60	3.06	4.97	0.06	0.01
		Profile 3			
In the same place	0-10	2.50	7.71	0.11	0.01
nearest to the Danube	10-20	2.41	7.59	0.08	0.01
(50 m from the road)	20-40	2.70	5.83	0.07	0.02
deep-lying soils	40-60	2.66	3.33	0.06	0.00
		Profile 4			
Near to the Danube	0-10	3.16	6.36	0.10	0.02
Near the road by	10-20	3.98	3.96	0.08	0.01
Nyergesújfalu	20-40	3.71	1.81	0.05	0.01
Alluvial meadow	40-60	2.28	0.90	0.03	0.01
chernozem	60-80	0.95	1.39	0.09	0.09
	80-100	0.30	2.17	0.11	0.06
		Profile 5			
Near to the Danube	0-10	1.68	4.40	0.08	0.34
Between the road and	10-20	1.42	4.02	0.08	0.23
the Danube	20-40	1.36	4.02	0.04	0.22
Almásfüzitő	40-60	1.22	2.84	0.03	0.23
Alluvial chernozem	60-80	1.01	0.86	0.04	0.36
		Profile 6			
Near to the lake of an	0-10	4.84	9.39	0.12	0.01
Electrical Power Plant	10-20	5.10	9.09	0.07	0.01
(West Hungary)	20-40	5.23	5.61	0.08	0.01
Groundwater level at	40-60	3.73	4.26	0.16	0.50
100 cm	60-80	2.32	3.20	0.13	0.56
	80-100	1.17	3.29	0.11	0.52
	100-120	0.47	3.44	0.12	0.65



Profile 4: meadow chernozem, Nyergesújfalu



Profile 5: alluvial meadow, Almásfüzitő



Profile 6: Near to the groundwater, Lake Bokod

Figure 1
Heavy metal distribution and mobility in soils (Influence of humus and groundwater). Profile 4: meadow chernozem, Nyergesújfalu; Profile 5: alluvial meadow, Almásfüzitő; Profile 6: Near to the groundwater, Lake Bokod

seen that besides organophility there is also a characteristic hydrophility, to a slight extent for Cd but not so characteristically as for Hg (see profiles 4, 5 and 6).

Another interesting characteristic picture is seen if we compare the organophility of Ni and Pb. In most cases Pb shows very strict organophility and at the highest level. The Pb accumulation is always greatest in the topsoil, in the surface humus layers (0-20 cm) or at a depth of 0-40 cm. In the case of Ni this organophility is not so pronounced. Between 0-40 cm it appears very slightly but in the deeper layers there is characteristically a considerable decrease in Ni contamination. All these characteristic distributions can be clearly seen in Figures 1 and 2.

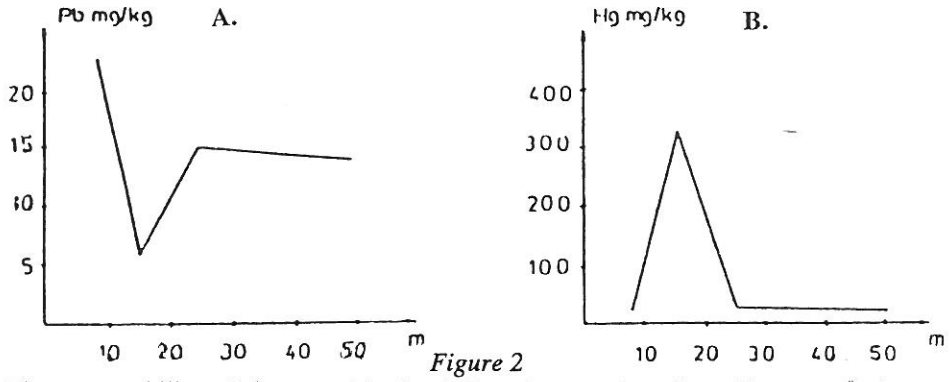


Figure 2

The organophility of Pb (A) and hydrophility of Hg (B) in soil profiles 5, 15 and 25 m from the highway

The distribution of Pb and Hg is compared in the profiles of two places not very far from each other beside one of the most important Hungarian highways (M-7) at distances of 57.5 and 74 km from Budapest. The contamination was investigated in both cases in successively situated profiles beside the road. At the 57.5 km site the second profile is on a very deep-lying meadow beside the road. Immediately next to the road is profile 1, 8 m from the highway. At this point which is nearest to the road and at the same level as the road, the Pb contamination is very high, while the Hg contamination is extremely low. At the deepest point of the profile 15 m from the road the Pb accumulation is not so important and was probably collected by the grasses and plants in the top layer, but the Hg contamination on the contrary, shows an outstanding maximum, indicating the hydrophility of Hg. Farther away, in a profile 25 m from the road, there is a relative increase in the Pb accumulation in the topsoil, while at 50 m from the road it also appears but not to such a high extent as beside the road. By contrast, in this last case (far away from the deep-lying profile) Hg exhibits a drastic decrease.

It seems that Hg, collected from the surface layers through precipitation, accumulates at the deepest point of the investigated area beside the road, mainly showing high contaminations near the groundwater level. The groundwater level is close to the soil surface in profile 2.

The character of the organophility of the investigated elements seemed to be very different. From these results and also from earlier results it seems that the highest level of organophility is exhibited by the charateristic distribution of Pb in the soil profiles. Pb always shows strong accumulation in soil humus layers.

For Ni this strict organophility is not so characteristic in the surface layers compared to the accumulation of Ni in the deeper layers. In our experience Ni accumulation should be considered from the point of view that Ni is very toxic to most plants, and so Ni accumulation cannot occur in raw organic materials because the plants are killed by Ni. Ni accumulation is only possible in plants in exceptional cases. So the retarding effect of plants is not so characteristic for Ni as for Pb.

The organophility of Cd is not so characteristic from another aspect and according to earlier results the organophility of Cd is only at third place among the toxic heavy metals, behind Pb and Ni. It is also well-known from many investigations and results on chemical speciation that Cd and Hg are very active in binding organic groups and developing metal-organic species.

The metal-organic species of Cd have similar character to the metal organic species by Hg. These organo-metallic compounds, such as dimethyl-Hg and dimethyl-Cd, are water-soluble, so their distribution in the soils and in the total environment is influenced by the groundwater level. Of course, their mobility is influenced, as a consequence of their chemical speciation, not only by their organophility but also to a very great extent by their hydrophility.

Soil contamination and the soil conditions are very similar in the soil profiles investigated. Due to this similarity the distribution of soil contaminants was investigated in three characteristic soil profiles at the 57.5 km site and in

Table 2

Characteristic distribution of organophilic heavy metals in soil profiles (Indices express the ratio of contaminants in the 0-20 cm layer compared to 20-40 cm)

Distance from the road	Distribution indices of contaminants					
	Pb		Ni		Cd	
	I.	II.	I.	II.	I.	II.
5 m	3.29	3.87	1.00	0.84	1.01	1.35
15 m	1.89	1.97	1.33	1.00	0.92	0.79
25 m	1.78	1.40	1.06	1.00	0.78	1.35

I. M-7 highway 57.5 km, II. M-7 highway 74 km from Budapest

other three profiles in the same line at the 74 km site. From the separate investigations of Pb, Ni and Cd contaminants in the soil layers in the two series of soil profiles a special index was calculated to characterize their organophility. This index expresses the ratio of contaminants (for the three organophilic elements) and provides information about the differences, scale and character of their organophility. The results are summarized in Table 2.

Besides organophility, the characteristic hydrophility, especially of Hg, also influences the movement of Hg not only in soil profiles but also in rivers and river sediments. Results concerning these relationships are summarized in Table 3.

Table 3

Distribution of Hg in alluvial chernozems of Danube sediments depending on the distance from the Danube, and Hg as contamination in river sediments of the Sajó

Profile site and distance from the Danube, m	Hg (mg/kg) in 0-60 cm	Sediments along the Sajó, in km	Hg (mg/kg) in 0-60 cm
Almásfüzitő (300)	0.400	Sajólád	0.785
Nyergesújfalu (500)	0.076	Sajópetri (1.5)	0.660
Ács (800)	0.006	Muhi (4)	0.060
		Nagycsécs (6)	0.022

From Table 3 it is clear that the industrial Hg contaminations collected by the Danube or by the River Sajó (North-East Hungary) show a characteristic dependence on the distance of the sources of contaminations along the river.

The movement and distribution of Hg and As are similar in character. Metal-organic compounds, such as the monomethyl and dimethyl forms of arsenic and mercury, play a very similar role. Biotransformational processes play an outstanding role in the methylation and dimethylation of As in water systems as well as in sediments.

The hydrophility of Hg and As are very characteristic and similar. In this connection investigations were made on the As contaminations in the South peatland area of the Great Hungarian Plain. The contamination with As in the profiles is to be seen in Table 4, which shows the distribution of As in the peat profiles investigated in this area. From the table it can be seen that in the distribution of As in peat profiles, as a very general rule, the highest values of As could be measured in peat layers near or below the groundwater level. Above this level As contamination shows a decrease, and at about 40-60 cm from the soil surface there is a minimum of As contamination over the whole territory. In the humified peat layers of the topsoil the As accumulation increases again, but not to such a great extent as in the layers affected by the groundwater level.

Table 4

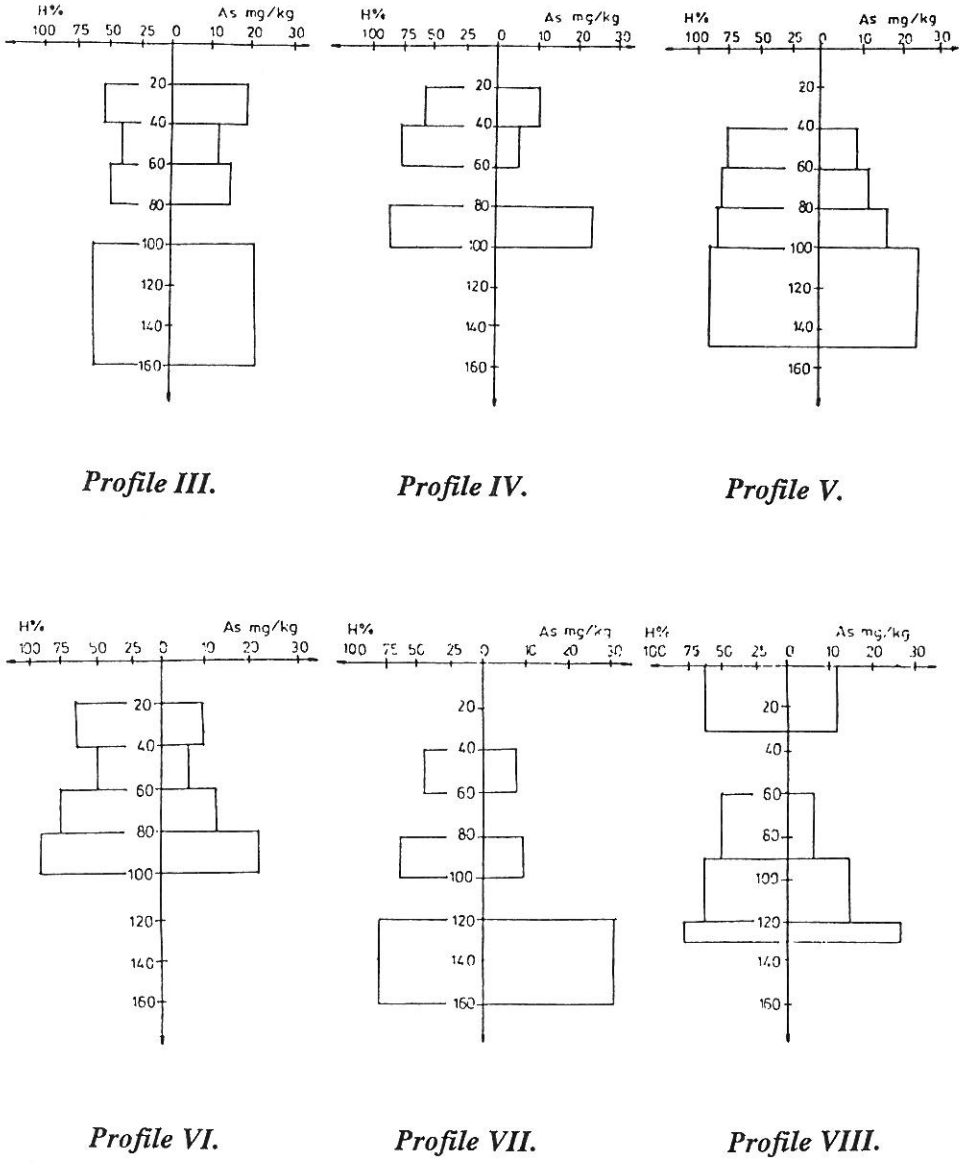
Distribution of As contamination in relationship with the groundwater table in a lowmoor peat area and the chemical parameters of the peats (South Hungary)

Peat layers	Organic matter content, %	$CaCO_3$, %	pH	As, mg/kg
Humified top layers	57.95	12.61	6.73	13.39
Raw peat layers	54.12	13.28	6.84	9.65
Layers near the groundwater level	76.31	3.50	6.57	21.42

Starting from these results, the behaviour of As seemed to be a very interesting question. The As contamination in Hungary is fairly high in certain regions. These As-contaminated territories are situated in the Central Southern area of Hungary. These As contaminations are of geological origin and appear mainly in the deep-lying peat areas of the southern part of the Great Hungarian Plain. The region investigated between the Danube and Tisza Rivers is a peat area consisting of very slightly acidic or near neutral peats. Arsenic is transported by groundwater streams from deeper geological layers mainly affected by weakly acidic pH. Arsenic moves in this case in the form of As^{III}, because the conditions are highly reductive, as O_2 is excluded in these water streams. It is in these groundwaters in the peat areas in South Hungary that As contamination appears. A rise in the groundwater level is the main reason for the appearance of relatively high As contaminations in the peat soils of this region.

Based on these results the effect of the total organic matter content in the peat layers on the movement and distribution of As in the peat profiles was investigated. The results can be seen in Figure 3. In the investigations the total organic matter content and As contamination values were compared from layer to layer, generally in each 20 cm in a strict sequence of layers. From these figures it can be clearly seen that in most cases the amount of As is relatively smaller at high H% (organic matter content) than at lower levels of H%. Another important result is that the As accumulation in organic materials is much greater in the vicinity of the groundwater level in each case.

In the present work, based also on previous results, investigations were carried out on the extent and character of the organophility of the most toxic elements, namely Pb, Ni, Cd, Hg and As. From the results the main conclusion was a confirmation of the characteristic organophility of Pb, Ni and Cd. Another conclusion was that the character of the organophility was different for each element. Pb and Ni are the most organophilic elements, but for Pb the accumulation is very strictly bound to the surface layers, while for Ni the char-



Profile III. *Profile IV.* *Profile V.*

Profile VI. *Profile VII.* *Profile VIII.*

Figure 3
Distribution of As in peat profiles influenced by total organic mater content and groundwater level (South Peatland Area of Hungary)

acter of distribution in the soil profiles is not the same. Cd is slightly organophilic.

As a second conclusion, it seems that with decreasing organophility there is an increase in the hydrophility of Cd. Hg and As are characterized by hydrophility. For these elements the phenomena of chemical speciation must also be expected. The behaviour of these toxic elements as regards their hydrophility is also different, because As is the most hydrophilic. Further investigations are needed to characterize the role of humic substances influencing their mobility. It seems that some processes of chemical speciation, and also the development of metal-organic complexes with humic and fulvic acids, have a great influence on their hydrophility as well as on their mobility in soils and sediments.

A general conclusion is that the ratio of well-humified organic matter in the soil layers is very important, as well as the total organic matter content. Since the most toxic elements are organophilic, their quantities in the soils were compared with the environment protectional capacity of the soils.

Since the ratio of well-humified humic substances in the layers is very important in the binding of the most toxic elements, the environment protectional capacity of the soils was calculated as EPC_G values. The EPC_G values consider not only the total humus content, but also the humus quality in the form of K values. The EPC_G values can be calculated from layer to layer (mainly to a depth of 60 cm). The differences in EPC_G values are very characteristic in soils with different humus status. The lowest EPC_G values are in the range of 10, and the highest in the range of 1000. This suggests that humus status may have a considerable influence on the binding of toxic elements. Since the most toxic elements are organophilic, if their quantities in the soils are compared with the environment protectional capacity, it is possible to characterize the risk of contamination at three main levels:

1. The highest risk is at high amounts of toxic heavy metals with low EPC_G values.
2. The medium level of risk is at moderate contamination with a medium range of EPC_G values.
3. The lowest risk is at a low level of contamination with high EPC_G values.

Summary

Since Goldschmidt's famous classic concept of the organophility of some heavy metals it is well-known that these elements are accumulated in the humus layers of soils.

In the present research, based on previous results, particular investigations were carried out on the extent and character of the organophility of the most toxic elements, such as Pb, Ni, Cd, Hg and As. At the same time, studies were made on the hydrophility of Cd, Hg and As. An attempt was made to express the rate of organophility by calculating the ratio of mobile amounts of Pb, Ni

and Cd in the 0-20 cm layer compared to their values in the 20-40 cm layer. In addition, their particular distribution in the sequence of the layers has been shown together with the distribution of the humus content in the same soil profiles. It was possible to characterize not only the rate but also the differences in the character of their organophility. It was also confirmed that the decreasing organophility of Cd and Hg is connected with increasing hydrophility. Accumulation in the deeper layers influenced by the groundwater level is characteristic of Hg and As. Hydrophility is the most characteristic of As contaminations; As accumulation is highest near to the groundwater level. The most dangerous As contaminations in Hungary are of geochemical origin, even in the investigated area. It seems that the mobility of Cd, Hg and As is deeply influenced by processes of chemical speciation through the development of organometallic complexes by Cd and Hg and also probably by complexes of Hg and As with humic and fulvic acids.

The processes investigated, concerning the influence of the amount of humic substances, seem to be very important, as does information on the role of humus quality in the mobility of these elements in the soil and in the environment.

References

BERNHARD, M., BRINCKMAN, F. E. & IRGOLIC, K. J., 1986. The importance of "chemical speciation" in environmental processes. Dahlem Konferenze. (Eds.: BERNHARD, M., BRINCKMAN, F. E. & SADLER, P. J.) 7-14. Springer Verlag. Berlin-Heidelberg.

GOLDSCHMIDT, V. M., 1937. The principles of distribution of chemical elements in minerals and rocks. Journal Chem. Soc. 665-673.

HARGITAI L., 1955. Összehasonlító szervesanyagvizsgálatok különböző talajtípusokon optikai módszerekkel. Agrártud. Egyetem Agron. Kar Kiadványa **2.** (10) 27. Mezőgazd. Kiadó. Budapest.

HARGITAI L., 1958. Néhány újabb kísérleti adat humuszsavak kémiai és fizikai-kémiai tulajdonságairól. Magyar Kémiai Folyóirat. **64.** 233-234.

HARGITAI L., 1983. A talajok környezetvédelmi kapcitásának meghatározása humuszállapotuk alapján. Agrokémia és Talajtan. **32.** 360-364.

HARGITAI, L., 1989. The role of humus status of soils in binding toxic elements and compounds. Sci. Total Environ. 81/82. 643-651. Elsevier. Amsterdam.

HARGITAI, L., 1990. The mobility of toxic heavy metals as affected by environment protectional capacity of soils. Trans. 14th Int. Congress Soil Science, Kyoto, Japan. Vol. II. 102-106.

LAKANEN, E. & ERVIÖ, R., 1971. A comparison of eight extractants for the determination of plant available micronutrients in soils. Acta Agr. Fenn. **123.** 223-232.

SCHUSTER, E., 1991. The behaviour of mercury in the soil with special emphasis on complexation and adsorption processes. Water, Air and Soil Pollution. **56.** 667-680.

WILKEN, R. D. & HINTELMANN, H., 1991. Mercury and methyl mercury in sediments and suspended particles from the river Elbe, North Germany. Water, Air and Soil Pollution. **56.** 427-437.

XU, H. & ALLARD, B., 1991. Effect of fulvic acids on the speciation and mobility of mercury in aqueous solutions. Water, Air and Soil Pollution. **56.** 709-717.

XU, H., ALLARD, B. & GRIMVALL, A., 1991. Effects of acidification and metal organic materials on the mobility of arsenic in the environment. Water, Air and Soil Pollution. **57-58.** 269-278.